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# CONTAMINATION OF SOILS WITH POLYCYCLIC AROMATIC HYDROCARBONS NEAR PETROL STATIONS IN THE CITY OF KIELCE

Petrochemical-derived products may enter the soil with rainwater, sewage, and during equipment failures. Due to their physicochemical properties, they cause a threat to the environment and change the properties of engineering-geological land. In the study, samples of soil originating from the vicinity of 20 gas stations in the city of Kielce have been examined. The following soil parameters were determined: pH, Hh, exchangeable cations, content of $CaCO_3$, $C_{org}$ and PAH. The amount of PAHs and their composition varied depending on numerous factors such as the soil quality as well as location and degree of exploitation of petrol stations.

## 1. INTRODUCTION

Transportation is one of the main drivers in economic development. Quick efficient and cost-effective transport of people and goods is a principal component of dynamic economy. No wonder that the number of cars has been increasing every year and with it the number of petrol stations. Each petrol station has to be equipped with appropriate safety systems and devices for protection of the environment from emission of petrochemicals and their vapors, including measurement and monitoring systems for control of fuel properties in tanks, and alarm systems for leaks and vapor emission. However, in spite of proper protective measures, the long-term operation of a petrol station in a particular location leads to gradual accumulation of contaminants in soils surrounding the station. Thus, the degree and rate of soil pollution with polycyclic aromatic hydrocarbons (PAHs) depends on popularity and capacity of the petrol station, land use in the surroundings and soil type.

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The main sources of soil pollution with petrochemicals include petrol stations, automobile service stations, port areas, etc. Petroleum products can penetrate into the soil with precipitation water, wastewaters and due to accidents. Because of their physicochemical properties, they are hazardous for the environment and can change geological and engineering land features [1]. Some PAHs are highly toxic, carcinogenic and mutagenic, and also highly stable in soil environment [2, 3]. PAHs migrate into the soil and can seal spaces through which water and air are transported, thus altering physical, chemical and biological properties of soils and posing a risk of worsening of water quality in the area [1]. In addition, productive features of soil deteriorate due to changes in microedaphone compositions. Depending on the mineral composition of soil, particle size distribution and degree of pollution, PAHs change such soil parameters as particle size and porosity, plasticity, density strength and compressibility. For these reasons, soils in the areas exposed to a direct impact of petrol stations should be constantly monitored.

Compounds belonging to PAHs are chemically stable. In soils, they undergo various abiotic transformations, i.e., sorption, leaching, reactions with other compounds, photodegradation [4] and very slow breakdown by fungi, bacteria and actinomycetes [5, 6]. Polycyclic aromatic hydrocarbons are soluble in organic solvents but only very slightly soluble in water. Too high contents of some PAHs in soils can negatively impact on soil organisms, and thus can change biodiversity and impair the habitat function of the soil [3, 7]. However, ecotoxicological threats from PAHs are variable and depend on their concentration and identity. For these reasons, information about concentrations of individual compounds and the whole group of PAHs is important for potential risk assessment to ecosystems and human health [1, 7].

European and Polish regulations set out requirements for minimizing PAH emission to the environment, including soils. The Federal Soil Protection and Contaminated Sites Regulation [7] stipulates three values to protect the soil from contamination: precautionary, test, and action values. The precautionary values are to prevent the occurrence of adverse soil alterations. If test values are exceeded, there are specific indications of an adverse soil alteration. The action values are meant to prevent risks in soils. There are values for the total of the 16 PAHs listed by the U.S. EPA and for the individual substances benzo[a]pyrene and naphthalene [8]. As for EU regulations, Annex X of the Water Framework Directive (2000/60/EC) (WFD) establishes a list of priority substances. This document sets environmental quality standards in EU for 33 priority substances, including eight PAHs [9].

Since PAHs have been included in the list of priority organic substances by the US Environmental Protection Agency (US-EPA 1994) [10, 11] and EC Water Framework Directive [12], they are among substances subjected to frequent monitoring [13]. In 2005 European Union adopted a list of PAHs (15 compounds) that have to be monitored in food and aquatic ecosystems [14].

Benzo(a)pyrene (BaP) is probably the most often tested PAH in environmental matrices. In 1987, International Organization for Research on Cancer (IARC) identified BaP as the main carcinogen in humans [15]. For this reason, BaP is commonly included in environmental analyses as a marker of the total content of PAHs. However, in many cases BaP constitutes only 1–20% of the total concentration of PAHs [13]. The maximum allowable concentration of benzo(a)pyrene in soil is 0.03 $mg\cdot kg^{-1}$ for type B land uses (agricultural, forest and bush soils, wasteland, residential, urban areas) and 50 $mg\cdot kg^{-1}$ for type C land uses (industrial areas, mining land, transportation areas) [16].

## 2. METHODS

Soil samples for determination of PAH contents were collected between April and May 2012 from 20 sites located in petrol station premises in the city of Kielce (Fig. 1). The petrol stations under study originated from the 1960s and 1990s and from the beginning of 2000. The stations had a daily capacity from 900 $dm^3$ (ca. 35–40 fill-ups per day) in stations No. 8 and 9 to 30 000 $dm^3$ (ca. 1000 fill-ups per day) in stations Nos. 1, 3, 6 and 14 (Table 1). A daily capacity of the remaining stations ranged from 400 000 to 9000 $dm^3$ (ca. 200 to 600 fill-ups per day). Usually petrol stations comprised a building with a service point, carwash, petrol pumps in the forecourt, 2–4 single or 2-chambered underground fuel tanks with a capacity of 5–50 $m^3$ and LPG tanks with a capacity of 3–8 $m^3$. Condition of buildings, petrol pumps and technical infrastructure differed between stations and depended mostly on duration of their use. Stations Nos. 8, 13, 19 and 20 were in poor technical state.

1 kg soil samples were collected randomly from the humic-mineral horizon to a depth of 25 cm with the use of an Egner's sampler. Every sample was a composite mixture collected radially from different directions of a biologically active area (covered with grass or ruderal vegetation) directly adjacent to each petrol station. The following soil parameters were determined in each soil sample: pH measured potentiometrically in soil suspension in 1 $mol\cdot dm^{-3}$ KCl and in $H_2O$, hydrolytic acidity *Hh*, exchangeable cations content ($K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$) in 1 $mol\cdot dm^{-3}$ $CH_3COONH_4$ (pH 7), content of $CaCO_3$, organic carbon ($C_{org}$) oxidized by the Tiurin method commonly used in pedology.

The contents of polycyclic PAHs (naphthalene acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene) in soils were determined using gas chromatography with mass spectrometry (GS-MS) on a Shimadzu GS-MS chromatograph QP 2010 Plus after extraction with dichloromethane according to a certified procedure in the IPIŚ PAN Laboratory in Zabrze.

After spiking the samples with an internal standard, soil samples of 1 g were extracted using ultrasound bath twice for 20 min, each time with 40 $cm^3$ of dichloromethane. The extract was concentrated to 1 $cm^3$ and purified on aluminum oxide/silica gel columns. The obtained eluate was concentrated again to 1 $cm^3$ and filtered through an injection PTFE filter. Samples prepared in that way were subjected to qualitative and quantitative chromatographic analyses. The analyses were carried out using programmed temperature increase in the range 80–280 °C. Samples were injected in the „split" mode 1:10. Limits of detection for analyzed compounds were from 0.004 mg·kg$^{-1}$ (dibenzo-(a,h)anthracene) to 0.022 mg·kg$^{-1}$ (fluorene, fluoranthene). Limits of quantitation ranged from 0.011 to 0.067 mg·kg$^{-1}$.

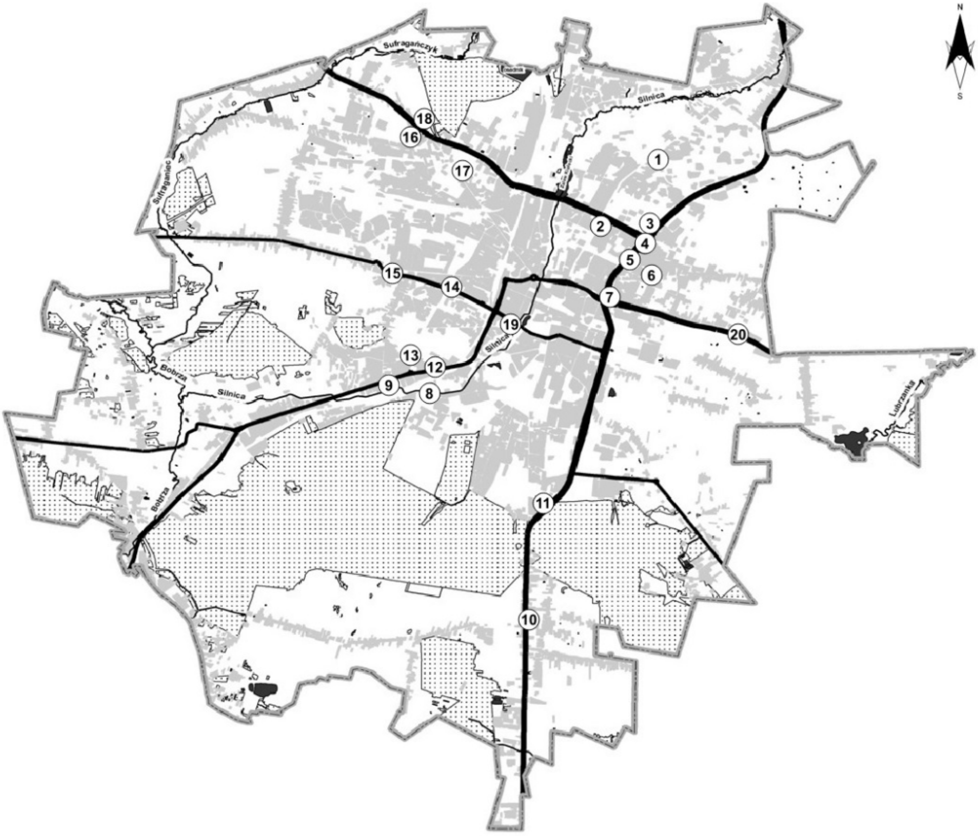

Fig. 1. Location of soil sampling sites (1–20) in the vicinity of petrol stations in Kielce

The obtained averaged values of contamination indices for individual PAHs were compared using an analysis of variance (ANOVA) preceded by a variance uniformity test of Brown–Forsyth. Data differing statistically significantly according to ANOVA, were further analyzed using the multiple comparisons Tukey test. ANOVA was also preceded by testing for normality of distribution with the use of the Kolmogorov–Smirnov test with the Lilliferosa correction and Shapiro–Wilk test. If the distribution was not normal, data were transformed according to function log*X*.

Table 1

Physicochemical properties of soil samples collected from the vicinity of petrol stations in Kielce

| No. | Station | Year start-up | pH in | | $V$ | $CaCO_3$ | $Hh$ | $K^+$ | $Na^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $S1$ | $T$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $H_2O$ | KCl | [%] | | [cmol(+)·kg$^{-1}$ d.m.] | | | | | | |
| 1 | Statoil, Warszawska | 1996 | 7.53 | 6.42 | 96.7 | 0.63 | 0.54 | 0.28 | 0.15 | 14.3 | 1.11 | 15.84 | 16.38 |
| 2 | Jet. Warszawska | 2000 | 8.37 | 7.85 | 90.8 | 0.05 | 1.33 | 0.25 | 0.17 | 12.3 | 0.56 | 13.28 | 14.61 |
| 3 | Orlen, Aleja Solidarności | 1962 | 8.91 | 7.54 | 99.5 | 0.05 | 0.18 | 0.31 | 0.08 | 10.3 | 0.29 | 11.0 | 11.05 |
| 4 | Schell, Manifestu Lipcowego | 2004 | 7.57 | 6.57 | 89.5 | 2.50 | 0.68 | 0.22 | 0.05 | 5.27 | 0.26 | 5.80 | 6.48 |
| 5 | BP, Manifestu Lipcowego | 2005 | 7.11 | 6.54 | 86.2 | 0.20 | 1.75 | 0.24 | 0.15 | 10.5 | 0.11 | 11.01 | 12.76 |
| 6 | Bliska, Domaszowska | 1962 | 7.31 | 6.62 | 97.5 | 0.89 | 0.26 | 0.21 | 0.10 | 9.64 | 0.19 | 10.14 | 10.40 |
| 7 | Statoil, Źródłowa | 1999 | 7.89 | 6.97 | 96.4 | 1.34 | 0.35 | 0.13 | 0.11 | 9.2 | 0.11 | 9.55 | 9.90 |
| 8 | Hurtex, Pakosz | 1961 | 8.32 | 7.88 | 97.0 | 1.65 | 0.44 | 0.21 | 0.2 | 13.1 | 0.98 | 14.49 | 14.93 |
| 9 | Autogaz, Krakowska | 1998 | 8.18 | 7.69 | 92.5 | 0.35 | 2.62 | 0.25 | 0.06 | 31.2 | 0.96 | 32.47 | 35.09 |
| 10 | Rolmet, Ściegiennego | 2004 | 8.02 | 7.18 | 99.8 | 9.95 | 0.07 | 0.18 | 0.03 | 46.2 | 1.36 | 47.77 | 47.84 |
| 11 | Orlen, Ściegiennego | 1945 | 8.41 | 7.97 | 96.4 | 0.94 | 0.67 | 0.25 | 0.16 | 16.3 | 1.60 | 18.31 | 18.98 |
| 12 | Orlen, Krakowska | 1965 | 8.16 | 7.93 | 92.6 | 0.97 | 0.92 | 0.26 | 0.04 | 10.7 | 0.49 | 11.52 | 12.44 |
| 13 | MPK, Jagiellońska | 1960 | 8.31 | 7.68 | 94.7 | 0.32 | 0.56 | 0.21 | 0.06 | 9.33 | 0.51 | 10.11 | 10.67 |
| 14 | BP, Jagiellońska | 2000 | 6.67 | 6.03 | 96.6 | 5.15 | 0.79 | 0.41 | 0.10 | 10.1 | 1.05 | 11.68 | 12.09 |
| 15 | Schell, Grunwaldzka | 2003 | 7.11 | 6.80 | 90.0 | 0.62 | 0.97 | 0.33 | 0.11 | 7.55 | 0.76 | 8.75 | 9.72 |
| 16 | Lotos, Łódzka | 2005 | 8.14 | 7.90 | 98.8 | 2.85 | 0.25 | 0.16 | 0.41 | 20.9 | 0.82 | 22.24 | 22.49 |
| 17 | Orlen, 1 Maja | 2000 | 6.97 | 6.75 | 97.8 | 7.52 | 0.70 | 0.70 | 0.22 | 32.3 | 1.54 | 34.71 | 35.46 |
| 18 | Orlen, Łódzka | 2000 | 6.11 | 6.05 | 94.7 | 0.0 | 0.44 | 0.70 | 0.21 | 6.12 | 0.98 | 8.01 | 8.45 |
| 19 | Orlen, Żytnia | 1999 | 6.01 | 5.66 | 79.08 | 0.0 | 1.32 | 0.44 | 0.09 | 3.84 | 0.62 | 4.99 | 6.31 |
| 20 | Orlen Sandomierska | 1964 | 8.07 | 7.77 | 98.7 | 1.87 | 0.18 | 0.33 | 0.20 | 12.6 | 0.91 | 14.05 | 14.23 |

*Hh* – hydrolytic acidity, *S*1 – sum of exchangeable cations, *T* – CEC, *V* – sorption complex saturation with bases.

Correlations between data were evaluated based on the slope of the line calculated by the least square regression method and a linear function was calculated based on Statistica ver. 10 Statsoft Polska. The correlation coefficient also demonstrates the direction of the association, therefore the Pearson's correlation coefficient was calculated. The significance level, i.e., probability of committing error of type I was assumed to be $\alpha = 0.05$ or $\alpha = 0.01$.

## 3. RESULTS AND DISCUSSION

The studies of soils collected from the premises of petrol stations were conducted from April to May 1012. PAHs never occur in the environment singly but form complex mixtures, the qualitative and quantitative composition of which depends on the type of combusted material and the combustion conditions [17]. PAHs occur in the ambient air as vapors or aerosols, most often deposited on dust particles.

Table 2

PAH content in the soil samples taken from the area of Kielce petrol stations [mg·kg$^{-1}$]

| PAH | Number of petrol station | | | | | | | | | | | | | | | | | | | | *MU* [%] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | |
| Naphthalene | <0.024 | <0.024 | <0.024 | <0.024 | 0.157 | <0.024 | <0.024 | 0.220 | <0.024 | <0.024 | 0.140 | 0.623 | <0.024 | <0.024 | 0.025 | <0.024 | <0.024 | <0.024 | <0.024 | 0.055 | 16.051 |
| Acenaphthylene | <0.056 | <0.056 | 0.153 | 0.147 | <0.056 | 0.150 | 0.161 | 0.164 | 0.159 | <0.056 | 0.143 | 0.155 | 0.190 | <0.056 | <0.056 | <0.056 | 0.156 | <0.056 | 0.167 | 0.152 | 18.917 |
| Acenaphthene | <0.018 | <0.018 | <0.018 | <0.018 | <0.018 | <0.018 | <0.018 | <0.018 | <0.018 | <0.018 | <0.018 | <0.018 | <0.018 | <0.018 | <0.018 | <0.018 | <0.018 | <0.018 | <0.018 | <0.018 | 16.162 |
| Fluorene | <0.039 | <0.039 | <0.039 | <0.039 | <0.039 | <0.039 | <0.039 | <0.039 | <0.039 | <0.039 | <0.039 | <0.039 | <0.039 | <0.039 | <0.039 | <0.039 | <0.039 | <0.039 | <0.039 | <0.039 | 18.341 |
| Phenanthrene | <0.016 | <0.016 | <0.016 | 0.169 | 0.039 | 0.111 | 0.181 | 0.149 | 0.149 | <0.016 | <0.016 | 0.051 | 0.342 | <0.016 | <0.016 | <0.016 | 0.050 | <0.016 | 0.364 | 0.069 | 18.503 |
| Anthracene | <0.095 | <0.095 | <0.095 | <0.095 | <0.095 | <0.095 | <0.095 | <0.095 | <0.095 | <0.095 | 0.101 | <0.095 | <0.095 | <0.095 | <0.095 | <0.095 | <0.095 | <0.095 | <0.095 | <0.095 | 19.167 |
| Fluoranthene | <0.029 | 0.037 | 0.039 | 0.361 | 0.089 | 0.221 | 0.667 | 0.600 | 0.456 | <0.029 | <0.029 | 0.163 | 1.110 | <0.029 | <0.029 | <0.029 | 0.213 | <0.029 | 1.546 | 0.290 | 17.559 |
| Pyrene | <0.028 | <0.028 | <0.028 | <0.028 | <0.028 | <0.028 | 0.502 | 0.556 | 0.038 | <0.028 | <0.028 | 0.127 | 0.857 | <0.028 | <0.028 | <0.028 | 0.211 | <0.028 | 0.9934 | 0.285 | 15.704 |
| Benzo(a)anthracene | 0.075 | 0.097 | 0.075 | 0.167 | 0.111 | 0.188 | 0.401 | 0..439 | 0.335 | 0.075 | 0.069 | 0.109 | 0.560 | 0.080 | 0.076 | 0.077 | 0.162 | 0.075 | 0.861 | 0.187 | 17.814 |
| Chrysene | 0.057 | 0.076 | 0.056 | 0.142 | 0.080 | 0.138 | 0.259 | 0.302 | 0.257 | 0.056 | 0.052 | 0.084 | 0.405 | 0.062 | 0.056 | 0.058 | 0.124 | 0.056 | 0.592 | 0.127 | 15.400 |
| Benzo(b)fluoranthene | <0.043 | 0.049 | <0.043 | 0.162 | 0.051 | 0.103 | 0.282 | 0.395 | 0.360 | <0.043 | <0.043 | 0.067 | 0.450 | <0.043 | <0.043 | <0.043 | 0.156 | <0.043 | 0.726 | 0.121 | 19.202 |
| Benzo(k)fluoranthene | <0.037 | <0.037 | <0.037 | <0.037 | <0.037 | <0.037 | 0.072 | 0.093 | 0.092 | <0.037 | <0.037 | <0.037 | 0.107 | <0.037 | <0.037 | <0.037 | <0.037 | <0.037 | 0.179 | <0.037 | 13.225 |
| Benzo(a)pyrene | <0.038 | <0.038 | <0.038 | 0.075 | <0.038 | 0.069 | 0.201 | 0.293 | 0.212 | <0.038 | <0.038 | 0.041 | 0.301 | <0.038 | <0.038 | <0.038 | 0.089 | <0.038 | 0.489 | 0.079 | 14.626 |
| Indeno(1,2,3-cd)pyrene | <0.031 | <0.031 | <0.031 | 0.039 | <0.031 | 0.049 | 0.149 | 0.248 | 0.247 | <0.031 | <0.031 | <0.031 | 0.229 | <0.031 | <0.031 | <0.031 | 0.094 | <0.031 | 0.415 | 0.046 | 16.372 |
| Dibenzo(a,h)anthracene | <0.034 | 0.321 | <0.034 | 0.312 | 0.316 | 0.324 | 0.330 | 0.347 | 0.331 | <0.034 | <0.034 | 0.326 | 0.338 | 0.322 | <0.034 | 0.324 | 0.330 | 0.318 | 0.345 | 0.319 | 18.899 |
| Benzo(g,h,i)perylene | <0.050 | <0.050 | <0.050 | <0.050 | <0.050 | <0.050 | 0.146 | 0.209 | 0.200 | <0.050 | <0.050 | <0.050 | 0.202 | <0.050 | <0.050 | <0.050 | 0.121 | <0.050 | 0.304 | 0.061 | 18.875 |
| Sum of 16 PAHs | 0.67 | 1.012 | 0.776 | 1.865 | 1.235 | 1.644 | 3.527 | 4.167 | 3.012 | 0.669 | 0.868 | 2.016 | 5.267 | 0.968 | 0.671 | 0.963 | 1.919 | 0.953 | 7.1574 | 1.98 | |
| Sum of 13 PAHs | 0.572 | 0.914 | 0.581 | 1.676 | 1.004 | 1.452 | 3.324 | 3.765 | 2.811 | 0.571 | 0.567 | 1.22 | 5.035 | 0.87 | 0.572 | 0.865 | 1.721 | 0.855 | 6.948 | 1.755 | |
| Sum of 9 PAHs | 0.427 | 0.482 | 0.436 | 1.245 | 0.71 | 0.999 | 2.256 | 2.702 | 2.088 | 0.426 | 0.538 | 1.283 | 3.489 | 0.437 | 0.428 | 0.43 | 1.034 | 0.426 | 5.001 | 1.084 | |

*MU* – measurement uncertainty.

In this way, emissions from traffic, e.g., produced by abrasion of rubber tyres or asphalt or by exhaust gases deposited on the road surface, and snowmelt runoff become enriched in PAHs, enter into the soil and then into the groundwater. PAHs can percolate through loose filtration soil horizons and migrate further, so they can be present in groundwater thus contaminating sources of drinking water.

PAHs occurring in soil environment can be of autogenic (formed in humification process) or exogenous origin (deposited with dust from fossil fuel and biomass combustion) [1, 18]. Hence, their contents show wide variability depending on the location and soil type and use [19, 20]. PAH contents in soils exposed to heavy traffic emissions (Table 2) confirmed the results obtained by Adamczewska et al. [19].

Analysis of the obtained data revealed that a half of soil samples collected from petrol stations was characterized by exceedance of the allowable limit for type B land use [16] and no exceedance of the allowable limit for type C land use in relation to residential and urban areas (Table 2). However, considering that the city of Kielce is situated within the area of the Main Groundwater Reservoirs (MGRs) which are the source of drinking water for the population, acceptance of the upper limit is not recommended due to the propensity of BaP to migrate to groundwater and the risk of its contamination. It is noteworthy that MGRs in the Kielce agglomeration are characterized by small resistance to contamination due to numerous surface outcrops of basement rocks and discontinuous cover of overlying permeable and semi-permeable quaternary sediments.

Table 3

Permissible content of PAHs in soils [$mg \cdot kg^{-1}$] [23]

| PAH | Group A | Group B | Group C |
|---|---|---|---|
| Naphthalene | 0.1 | 0.1 | 50 |
| Phenanthrene | 0.1 | 0.1 | 50 |
| Anthracene | 0.1 | 0.1 | 50 |
| Fluoranthene | 0.1 | 0.1 | 50 |
| Benzo(a)anthracene | 0.1 | 0.1 | 50 |
| Chrysene | 0.1 | 0.1 | 50 |
| Benzo(a)fluoranthene | 0.1 | 0.1 | 50 |
| Benzo(a)pyrene | 0.02 | 0.03 | 50 |
| Benzo(g,h,i)perylene | 0.1 | 0.1 | 50 |
| Sum of PAHs | 1 | 1 | 250 |

According to guidelines [16], soil or ground is classified as polluted if the concentration of at least one substance exceeds allowable limit (Table 3). Therefore, PAH concentrations in soil samples collected in petrol stations in the city of Kielce did not exceed allowable limits for type B land use for any compound only at eight sampling sites Nos. 1–3, 10, 14–16 and 18. In the remaining petrol stations, allowable limits were exceeded at least for two PAHs. PAH concentrations in none of the samples exceeded allowable quality standards for type C land use.

The contents of nine PAHs (naphthalene, fenanthrene, anthracene, fluoranthene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, bezno(a)pyrene, benzo(g,h,i)terylene) showed wide variability between sampling sites ranging from 0.426 to 5.001 mg·kg$^{-1}$, with a mean of 1.296 mg·kg$^{-1}$. In samples from nine petrol stations, the sum of nine PAH concentrations exceeded allowable limit of 1 mg·kg$^{-1}$ according to the Regulation of the Minister of the Environment Concerning Soil and Ground Quality Standards (Poland) [20], above which soils are classified as polluted. Samples collected from site No. 19 showed the heavies pollution with the highest content of the sum of nine PAHs.

Table 4

Classes of soil contamination with PAHs [µg·kg$^{-1}$] of IUNG [1]

| PAH contamination in soil | Degree of pollution | Assessment of soil contamination |
|---|---|---|
| <200 | 0 | not contaminated (natural content) |
| 200–600 | 1 | not contaminated (increased content) |
| 600–1000 | 2 | weakly contaminated |
| 1000–5000 | 3 | contaminated |
| 5000–10000 | 4 | heavily contaminated |
| >10000 | 5 | very heavily contaminated |

The contents of 13 PAHs (fluorene, fenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)-pyrene, dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene, benzo(g,h,i)terylene) in all soil samples ranged from 0.5670 to 6.9484 mg·kg$^{-1}$, with a mean of 1.8539 mg·kg$^{-1}$. Soils in petrol stations Nos. 1, 3, 10, 11 and 15 showed the elevated sum of 13 PAH contents corresponding to the first degree of contamination according to IUNG classification (Table 4) (uncontaminated soils), while petrol stations Nos. 2, 14, 16 and 18 were characterized by the sum of 13 PAH content corresponding to slight soil contamination (2nd degree). The maximum sum of13 PAH content, corresponding to the 4th degree of contamination and indicating heavy contamination of soil was noted in stations Nos. 13 and 19. The remaining 9 petrol stations were situated on contaminated grounds, i.e., classified as the 3rd degree of contamination.

The contents of 16 PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, fenantrene, fluorantene, pyrene, benzo(a)anthracene, chrysene, benzo(b)--fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, indeno (1,2,3-cd)pyrene, benzo(g,h,i)perylene) in all soil samples ranged from 0.6690 to 7.1574 mg·kg$^{-1}$, with a mean of 2.0670 mg·kg$^{-1}$ (Table 2).

All soil samples from petrol stations demonstrated the sum of 16 PAH content higher than 0.6 mg·kg$^{-1}$, i.e., they belonged to moderately and heavily contaminated soils. Soils from sampling sites Nos. 1, 3, 10, 11, 14, 15, 16 and 18 showed the sum of 16 PAH content corresponding to medium soil contamination. The maximum sum of 16 PAH content indicative of strong soil contamination was noted at the remaining 12 sampling sites, with soil samples collected in petrol station Nos. 13 and 19 being the most contaminated.

It should be emphasized that regardless of the classification system (system of IUNG Puławy or Regulation of the Minister of the Environment Concerning Soil and Ground Quality Standards or US Environmental Protection Agency, or other) , the highest soil contamination was evidenced in the MPK petrol stations (sampling sites Nos. 13 and 19, respectively), while the least contaminated were soils in the Statoil petrol stations (sampling sites Nos. 1 and 10).

In order to determine which stations are similar (or different) in terms of the content of PAH in soils, Tukey's test was used. The test was performed to group fuel stations, and to show differences between them. As evidenced by our results (Table 5), the contents of individual PAHs in soils from petrol stations, both with respect to structure and the proportion of individual PAH, is different for each petrol station. The results indicate that the contents of PAHs differed depending on, e.g., soil quality, fuel composition, land use, land management, proximity of expressways, number of cars and trucks served per day, availability of other services, e.g., car wash. The contents of benzo(b)fluoranthene showed the greatest variability and could be divided into 8 groups (Table 5), five of which (4–8) contained only one location. Whereas two groups (2nd and 3rd) comprised two petrol stations each, characterized by the same level of contamination with benzo(b)fluoranthene (Table 5).

For such compounds as naphthalene, fluorene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene variance was not uniform. Depending on the compound, two or more uniform groups were distinguished based on the mean values of individual compounds in soil samples collected at different sites. It can also be noticed that some petrol stations are included into two or more groups with reference to one compound, e.g., site No. 11 (Orlen petrol station) was categorized into group 1 and 2 based on acenaphthylene, while site No. 16 (Lotos petrol station) into group 2, 3 and 4 based on dibenzo(a,h)anthracene, which indicates that mean contents of these compounds in soil samples from different stations did not differ significantly.

Soil samples differed in composition with respect to individual PAHs in terms of the number of aromatic rings in their structure (Fig. 2) and the build of individual PAHs is very important for stability, i.e., their low susceptibility to biotic and abiotic degradation depends on the structure and properties of individual hydrocarbons. It was demonstrated that the greater the number of rings, i.e., the higher the molecular weight is, the lower the degradation rate [21]. The stability of tetracyclic PAHs in soils increases in the following order: chrysene > pyrene > fluorene > anthracene [22]. The lowest contents of chrysene were observed in samples from site No. 12, pyrene – from site No. 14

and anthracene – from site No. 19. It is associated with increased hydrophobicity of PAHs and their stronger adsorption in soils [23], and with the greater resistance to microbiological attack. Poor solubility in water, low compressibility of vapor and aromatic character cause that compounds of this group of contaminants demonstrate high affinity for solid surfaces. Therefore, it is thought that PAHs occur in the environment adsorbed on the surface of solid particles, however, it is relevant mostly to tetra- or more cyclic PAHs [24].

Table 5

Division into groups according to the comparable PAH content
(based on the HSD Tukey test, individual groups, $\alpha = 0.05$, $df = 40\ 000$

| Compound (Error: MS intergroup) | Group | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Acenaphthylene (0.00014) | 1, 2, 18, 16, 5, 15, 14, 10, 11 | 11, 4, 6, 20, 3, 12, 17, 9, 7, 8, 19 | 3, 12, 17, 9, 7, 8, 19, 13 | | | | | | |
| Phenanthrene (0.00008) | 1, 2, 3, 18, 16, 15, 14, 11, 10, 5 | 5, 17, 12 | 17, 12, 20 | 6 | 9, 8, 4 | 4, 7 | 13, 19 | | |
| Chrysene (0.00004) | 11, 3, 15, 10, 1, 18, 16, 14 | 1, 16, 14, 2 | 14, 2, 5 | 2, 5, 12 | 17, 20, 6, 4 | 9, 7 | 8 | 13 | 19 |
| Benzo(b) fluoranthene (0.00007) | 1, 18, 3< 15, 14, 11, 10, 16, 2, 5, 12 | 6, 20 | 17, 4 | 7 | 9 | 8 | 13 | 19 | |
| Benzo(k) fluoranthene (0.00005) | 1, 2, 3, 4, 18, 6, 16, 15, 12, 11, 20, 5, 17, 14, 10 | 7, 9, 8 | 9, 8, 13 | 19 | | | | | |
| Benzo(a) pyrene (0.00007) | 1, 2, 3, 16, 5, 15, 11, 18, 10, 14, 12 | 6, 4, 20, 17 | 7, 9 | 8, 13 | 19 | | | | |
| Dibenzo(a,h) anthracene (0.00008) | 1, 15, 3, 11, 10 | 4, 5, 18, 20, 2, 14, 16, 6, 12, 7, 17, 9, 13 | 18, 20, 2, 14, 16, 6, 12, 7, 17, 9, 13, 19 | 2, 14, 16, 6, 12, 7, 17, 9, 13, 19 | | | | | |

Most pentacyclic PAHs (45–46%) were observed at sites Nos. 2, 14, 16 and 18, i.e., Petrol stations Nos. 2, 16 and 18 are located at an exit road from the city connecting it with the city of Łódź, and at the station No. 14 located at an exit road to Częstochowa. Such locations cause that more cars and trucks are served there, contributing to the increased emission of contaminants which due to their stability, accumulate in soil. Weiss et al. [6] as well as Wilcke and Amelung [4] reported that high contents of some PAHs, like pyrene and chrysene, i.e., tetracyclic compounds, evidence environmental impact of human activities [22]. The greatest amount of tetracyclic PAHs (42–47%) occurred at stations Nos. 7, 8, 13 and 19. These petrol stations are located at streets connecting to an exit to the road proceeding from Kielce towards Kraków.

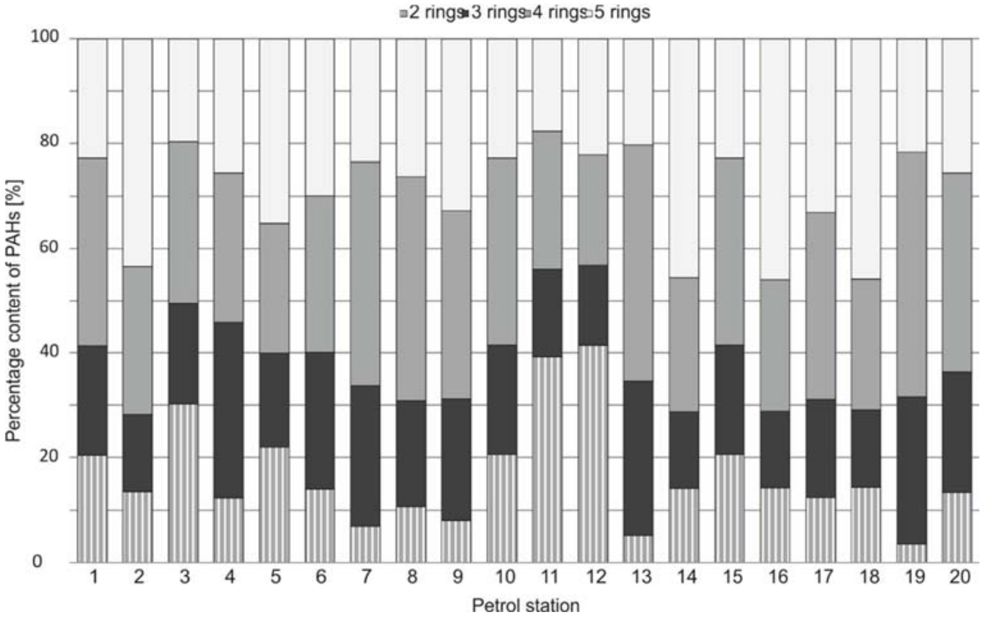

Fig. 2. Relationship between percentage content of PAHs and the number of aromatic rings in their structure in soil samples from petrol stations under investigation

Soil samples collected from stations No. 13 and 19 were characterized by a similar composition of the remaining compounds: bicyclic 3.5–5%, tricyclic 28–30%, and pentacyclic 20–22%. These soils belonging to most contaminated by PAHs contained the lowest amounts of bicyclic compounds of all analyzed petrol stations while soils from station No. 11 and 12 belonging to PNK Orlen showed the highest content of bicyclic PAHs reaching 40%. Similar results reported Abbas and Brack [25] who studied soil samples from Ughelli West, Tanker Loading point and Delta Steel Company, which is indicative of petrogenic origin. Nganja et al. [26] however, who examined the samples of surface soils, collected from petroleum handling facilities (kerosene tank, generating plant, petrol stations, mechanic workshops and others) from Calabar metropolis south-eastern Nigeria found that two- and three ring aromatic hydrocarbons predominated in soil samples [26].

Chemical analysis of soil samples demonstrated wide variability of the degree of soil acidification and alkalization. Hydrolytic acidity *Hh* of soil samples describes a potential soil acidity and is connected with hydrogen ($H^+$) and aluminum ions ($Al^{3+}$) of sorption complex and soil solution. This parameter is a measure of saturation of sorption complex of soils with hydrogen and comprises total acidity. Soil samples collected from stations Nos. 2, 5, 9 and 19 were characterized by the highest values of *Hh*, however, despite that hydrolytic acidity is closely connected with hydrogen $H^+$ ion content, a significant correlation between these parameters was not obtained. Soil samples with the lowest pH in water (6.01–6.11) originated from sites No. 19 and 18, respectively, but only at site 19 high *Hh* corresponded to low pH. On the other hand, the highest pH (8.91) was noted for soils from station No. 3 where hydrolytic acidity was 0.44 $\text{cmol}(+)\cdot\text{kg}^{-1}$, which was not much different from the mean value. Soil samples from station No. 19 were also characterized by the highest contamination with PAHs. Similar relationships were obtained from the analysis of the relation between pH in KCl solutions and soil contamination with PAHs.

The presence of strongly acidic ($H^+$, $Al^{3+}$) and strongly basic ($Ca^{2+}$, $Mg^{2+}$, $K^+$, $Na^+$) cations constitutes sorption complex of soils. Exchangeable basic cations can be absorbed by plants after being dissolved in soil solution while the presence of divalent basic cations positively influences soil structure. The results of the present analysis demonstrated the same tendencies within the groups of monovalent and divalent cations. $Ca^{2+}$ content was on the average 14 times greater than that of the remaining basic cations. It was associated with the contents of calcium carbonate, which was confirmed by a high value of correlation coefficient equaling 0.7398 which indicated a strong relationship between these parameters.

Strength of the association expressed by the correlation coefficient can be classified according to its value as follows:

- no association 0–0.2,
- weak 0.2–0.4,
- medium 0.4–0.7,
- strong 0.7–0.9,
- very strong 0.9–1.

A strong association (correlation coefficient 0.74) was also obtained for the sum of exchangeable cations (S1) and $Ca^{2+}$ ions, and for S1 and $CaCO_3$ which substantiates the significance of calcium ions for determining the character of soils in the city of Kielce. In difference, the association between calcium cations and sorption complex saturation with bases (V) was weak (correlation coefficient of ca. 0.42). In soils with an alkaline reaction, calcium carbonate is decisive for their buffering capacities in response to pH changes. Importantly, alkaline reaction resulting from the presence of carbonates has soil structure building capability and is favorable for the formation of stable organic substances and humus accumulation.

The contents of individual PAHs are significant for quality of the environment. In temperate climate, in which Poland is situated, when temperature is high, light substances evaporate while the remaining compounds sink into the ground. The compounds shatter physicochemical properties of soils, including their colloidal systems. Their presence reduces ion exchange and water absorption and desorption by soil colloids which negatively impacts sorption capacity. Literature reports also indicate that alkalization of the environment can be a result of seasonal decomposition of organic compounds [27].

Chemical reactions of PAHs can be divided into two groups: substitution and addition in which unsaturated bonds are destroyed. These hydrocarbons are sensitive to light, oxygen, ozone and other oxidizers. In the presence of light and oxygen, PAHs enter photochemical reaction yielding diols, quinines and aldehydes as final products. These properties are very important for attempts to eliminate these contaminants from the environment [27]. For these reason, it would be recommended to implement appropriate measures to remove PAHs accumulated in soils. However, considering the fact that petrol stations are located above the main groundwater reservoirs, it would be advisable to use biological methods, e.g., phytoremediation, which allows not only for improvement of soil quality but also contributes to purer air and better visibility.

## 4. CONCLUSIONS

Traffic is one of the main sources of emissions hazardous for natural environment, and for health and even life of people. Operation of petrol stations generates emissions containing, beside heavy metals and particulate matter, also hydrocarbons, including polycyclic aromatic hydrocarbons.

The present analysis demonstrated soil contamination with petrochemicals in petrol stations located within the boundaries of the city of Kielce and exceedance of allowable limits. The amount and composition of PAHs were diverse and depended on many factors like soil quality parameters, location of capacity of the petrol station. What is important, the PAH content is not dependent on the source of fuel, because the soil samples taken from the petrol stations belonging to the same company but in different locations of Kielce (such as Orlen or Statoil or others) have different characteristics. Therefore, each petrol station should be considered individually, both in terms of pollution and measures taken for the rehabilitation. It should be highlighted that due to the situation of the city of Kielce on top of major groundwater aquifers (MGRs) soil contaminated with petrochemicals should be reclaimed using methods based on biological processes, most of all by phytoremediation.

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